The polarized Raman spectra of the upper part of a thin ice Ih film were obtained in the range of 150 cm$^{-1}$ to 3800 cm$^{-1}$. The spectra showed clear polarization dependence; several new peaks were also observed. The longitudinal-optic–transverse-optic (LO–TO) splitting of the mode near 220 cm$^{-1}$ in the translational vibration region was experimentally confirmed at 133 K. The Fermi resonance between the bending overtone (around 3270 cm$^{-1}$) and symmetry stretching fundamental (around 3350 cm$^{-1}$) in the stretching vibration region appeared at nearly the same temperature. Results showed that ice XI (i.e., proton-ordered phase of ice Ih) slowly formed in the upper part of a thin ice Ih film without KOH as the temperature gradually decreased below 133 K.

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Keywords: ice Ih; ice XI; LO–TO splitting; Fermi resonance

Introduction

Ice Ih, the normal form of ice, had been extensively investigated since the pioneering work of Bragg in 1922. Ice Ih is built from water molecules arranged on a tetrahedral lattice [P6$_3$/mcc(D$_6^h$)], subject to a set of rules known as ice rules. These rules allow for orientational disorder of molecules, which is discussed in terms of positional disorder of H atoms, known as proton disorder. Under ambient pressures, ice Ih is in its stable phase at ~72 K. Below this temperature, a proton-ordered (ferroelectric) phase, known as ice XI with orthorhombic symmetry [Cmc2$_1$(C$_{12}$$^1$)$_2$)], becomes the ground state. This state could be obtained by doping a small amount of KOH that accelerates proton rearrangement to ice Ih. However, Furic observed that ice XI$\leftrightarrow$Ih phase transition at 84 K for pure water promotes phase transition temperature.

In practice, the ordering transformation from ice Ih to the lowest total energy ice XI phase rarely occurs because proton motion stops as temperature decreases to transition temperature $T_c$. Pan et al. proposed a first principle determination of the surface energy of ice Ih and revealed that the ice surface is significantly more proton-ordered than bulk, suggesting that, under equilibrium, an ice Ih surface does not become fully proton-disordered at any relevant temperature.

The vibrational spectrum of crystalline ice Ih has been the object of numerous studies for many years. In contrast to ice Ih studies, spectroscopic studies on the ice XI phase are extremely rare because of the difficulty in growing a single crystal that is suitable for optical measurements.

The present study aims to observe how polarized Raman spectra of thin ice Ih film differ in proton ordering from 253 K to 83 K. Sample preparation and experimental conditions are briefly described, and the Raman spectra of the upper part of a thin ice Ih film in the translational vibration range and OH stretching vibration are studied. The LO–TO splitting of the strongest mode near 220 cm$^{-1}$ and the Fermi resonance between the bending overtone and symmetry stretching fundamental are obtained below 133 K. These phenomena indicate that ice XI slowly grows in the thin ice Ih film as temperature continuously drops.

Experiment

Ultrapure and HPLC-grade water was purchased from Alfa AesarCo. An ice film was grown on the surface of a quartz single crystal. The ice Ih was crystalline, whose thickness was measured with a microscope on a Raman spectrometer. The ice sample was excited by an Arion laser at 5145 Å and an output power of 13 mW. The Raman spectrum in backscattering configuration was obtained using a 50x long working distance objective lens located on the ice surface. With a working distance (WD) of 17 mm, the investigated volume was located at around the probing depth of 10 μm from the surface, providing an insight into the film properties of ice [Fig.S1 (Supporting Information)]. All spectra were obtained at a scanning speed of 10 cm$^{-1}$/min. A 1200 lines/mm grating was used, which provided 4 cm$^{-1}$ spectral resolution. The Raman spectra were obtained using a Renishaw InVia Raman spectrometer. The spectra at low temperature were obtained using a Thmsg Linkam...
thermal PE95 system at a temperature range of 77 K to 873 K with 0.1 K accuracy. Each temperature interval lasted for 10 min after collecting the spectrum.

Results and discussion

The intensity of Raman scattering radiation polarized parallel to the incident light \( I_{VV} \) and perpendicular to the incident light \( I_{VH} \) in the translational vibration and OH stretching regions were separately measured. The spectra in the thin ice film showed clear polarization dependence; several new peaks were also observed.

Figure 1(a) shows the Raman shift variation exhibited by spectra \( I_{VH} \) in the translational vibration at various temperatures. Both the Raman shifts at around 220 and 300 cm\(^{-1}\) monotonically softened within the temperature range of 83 and 253 K because the intermolecular van der Waals bond as OH (\( \omega_L \sim 200 \text{ cm}^{-1} \)) bond [10] contracted with decreasing temperature. This behavior resulted in continuous decrease in \( \omega_L \) within the temperature range of the ice phase [11].

The nucleation process started on the surface and spread into the center of the ice, which lasted a long period [12]. Transformation to ice XI over a whole sample area was not possible. Therefore, the laser beam must be scanned to identify the well-transformed parts of the sample. Figure 2 shows the Raman spectrum of the upper part of the thin ice film. This part of the spectrum showed that the 220 cm\(^{-1}\) peak was stronger and split into 215 and 222 cm\(^{-1}\) at 113 K. Another typical feature in the translational spectra was the peak shift at around 320 cm\(^{-1}\) to higher frequency side [Fig. 1 (b)]. These results indicated that this part exhibited the ice XI structure molecules. Abe and Shigenari [13] assigned the peak observed at high Raman shift as the LO mode with mixed symmetry of \( A_1/B_2 \) and the peak at low Raman shift as the TO mode with mixed symmetry of \( A_2/B_1 \). The estimated LO–TO splitting was observed at about 6.0±0.5 cm\(^{-1}\). This value was close to the obtained data of splitting by 7.0 cm\(^{-1}\). The LO–TO splitting of the mode near 220 cm\(^{-1}\) illustrated that the long range force effect appeared distinctly in ice XI. However, only a weak 223 cm\(^{-1}\) peak was observed in the center of the sample at 93 K, in which ice \( I_h \) existed, whereas ice XI was not observed (Fig. 1 (b)).

Figure 3 shows the polarized Raman spectrum \( I_{VH} \) in the range of 2700 and 3800 cm\(^{-1}\) of the upper part of thin ice film at 253 K to 83 K. A temperature decrease induced decrease in the intensity of the region around 3350 cm\(^{-1}\). This region corresponds to symmetric OH stretching—\( \nu_s \) [14,15], an increase in the intensity of the region around 3120 cm\(^{-1}\) was also observed. This region corresponds to asymmetric OH stretching. The shoulder peak, \( \nu_{as} \), which is the overtone of the bending modes, was initially located at around 3270 cm\(^{-1}\). The intensity of this peak gradually increased with decreasing temperature. Below 133 K, the intensity of the peak rapidly increased. The intensities of the \( \nu_- \) and \( \nu_+ \) peaks changed in opposite directions with decreasing temperature. The \( \nu_- \) peak shift gradually decreased; whereas, the height of the large peak at 3326 cm\(^{-1}\) increased at 133 K. Finally, the original large peak decreased to a shoulder at 83 K. These two peaks are associated with the resonant states formed by the mixing of stretching and overtone of the bending modes (Fig. 4). A significant initial growth in population of the \( |0, 2 \rangle \) state is expected from the harmonic coupling between the two modes [16] consistent with the experimental results. The Raman intensity successively
moved from a high-wavenumber to a low-wavenumber peak, while their separation remained constant. This behavior is typical of Fermi resonance.\textsuperscript{17–19}

Variations from ice I\textsubscript{h} to ice XI, except for the intensity increase, were not significant in the stretching modes.\textsuperscript{20} The changes are attributed to Fermi resonance between $v_{\text{r}}$ and $v_{\text{r}}+\nu$ modes in ice XI.

Figure 5 shows the variation of the $v_{\text{r}}$ and $v_{\text{r}}+\nu$ wavenumbers of the coupled states with temperature. The $v_{\text{r}}$ wavenumber decreased up to 133 K, which agreed with the previous results.\textsuperscript{21} Remarkable resonant behavior was observed at temperatures below 133 K. At around 133 K, the $v_{\text{r}}$ wavenumber reached a minimum and then increased; whereas, the temperature-insensitive $v_{\text{r}}$ wavenumber started to rapidly decrease. These phenomena indicated that ice XI was gradually generated in the upper part of the thin ice film when the temperature was below 133 K; this temperature was higher than the result obtained by Furi\'ć.\textsuperscript{5} The content of ice XI was observed in the upper part by Raman technique at 133 K. Longer period is needed to form enough ice XI when the temperature is higher than 133 K.\textsuperscript{22} However, the Raman spectra for the center of the thin ice film did not change.

### Conclusion

The polarized Raman spectra of the upper part of a thin ice I\textsubscript{h} film without KOH showed the characteristic peaks of ice XI when the temperature was below 133 K. The LO–TO splitting and Fermi resonance formed in ice I\textsubscript{h} indicated that ice XI$\Leftarrow$I\textsubscript{h} phase transition was generated without KOH. Ice XI first appeared on the surface of ice I\textsubscript{h} and spreads to the center. The phase $T_c$ may not be a constant value; thus, the Raman spectrum of a few ice XI structures in ice I\textsubscript{h} could not be obtained when temperatures are higher than 133 K.

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### References

Proton order of thin ice Ih film


Supporting Information
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